ISSN 2176-3135

COMPARISON OF TECHNOLOGIES FOR DESULPHURISATION OF COKE OVEN GAS[1]

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Abstract

Coke Oven Gas (COG) contains hydrogen sulphide (H_2S) and other sulphuric compounds like carbon disulphide (CS_2), carbonyl sulphide (COS), mercaptans etc. The separation of these pollutants is strongly required by environmental protection. Generally the processes suitable for desulphurisation of coke oven gas can be subdivided into different methods: dry oxidation processes; wet oxidation processes; absorption/stripping processes. In the following paper only the wet oxidation and the absorption / stripping processes will be considered for comparison as they form the main types of desulphurisation processes for COG cleaning. The common by-products from these cleaning processes are: elementary sulphur; ammonium sulphate; sulphuric acid. This paper provides an overview of the most common desulphurisation processes and elaborates on the differences. Further the desulphurisation processes are compared in terms of technical process routes, environmental matters and Total Cost of Ownership (TCO), followed by a conclusion.

Key words: Desulphurisation; Coke oven gas; Environment; Emissions.

COMPARAÇÃO DAS TECNOLOGIAS PARA DESSULFURAÇÃO DE GÁS DE COQUERIA

Resumo

O Gás de Coqueria contém ácido sulfídrico (H2S) e outros compostos sulfúricos como dissulfeto de carbono (CS2), sulfeto de carbonila (COS), mercaptanos, etc. A separação desses poluentes é fortemente exigido pela proteção ambiental. Geralmente os processos adequados para dessulfurização de gás de coqueria podem ser subdivididos em métodos diferentes: processos de oxidação a seco; processos a úmido de oxidação; e processos de absorção/ *stripping*. No presente trabalho apenas a oxidação úmida e os processos de absorção/ *stripping* serão considerados para a comparação, uma vez que eles formam os principais tipos de processos de dessulfuração para limpeza COG. Os produtos comumente obtidos a partir destes processos de limpeza são: enxofre elementar; sulfato de amônio; e ácido sulfúrico. O trabalho fornece uma visão geral dos processos de dessulfuração mais usuais e aborda as principais diferenças, comparando os processos em termos de fluxogramas, questões ambientais e Custo Total de Aquisição (TCO).

Palavras-chave: Dessulfuração; Gás de coqueria; Meio ambiente; Emissões.

[1] *41st Ironmaking and Raw Materials Seminar & 12th Brazilian Symposium on Iron Ore, ABM, September 12-15th 2011, Vila Velha (Grande Vitória), ES, Brazil.*

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ISSN 2176-3135

1 INTRODUCTION

Because of its hydrogen sulphide (H_2S) content (up to 9 g/Nm^3) unpurified coke oven gas is unsuited for use in many industrial applications. When the gas has been desulphurised, however, its use for a variety of applications becomes potentially viable.
Many coke plants meanwhile sell coke oven gas after desulphurisation at a profit. Desulphurisation for commercial reasons coincides with the need to protect the environment from the effect of acid rain, because desulphurised coke oven gas decreases emissions of SO_2 at the site of coke oven gas combustion. COG desulphurisation is becoming increasingly common practice in the European Union due to the environmental legislation in force.
However, depending on the final utilisation (Figure 1) the grade of COG cleaning may differ distinctly (Table 1) and will have an impact on the selection of the desulphurisation process.

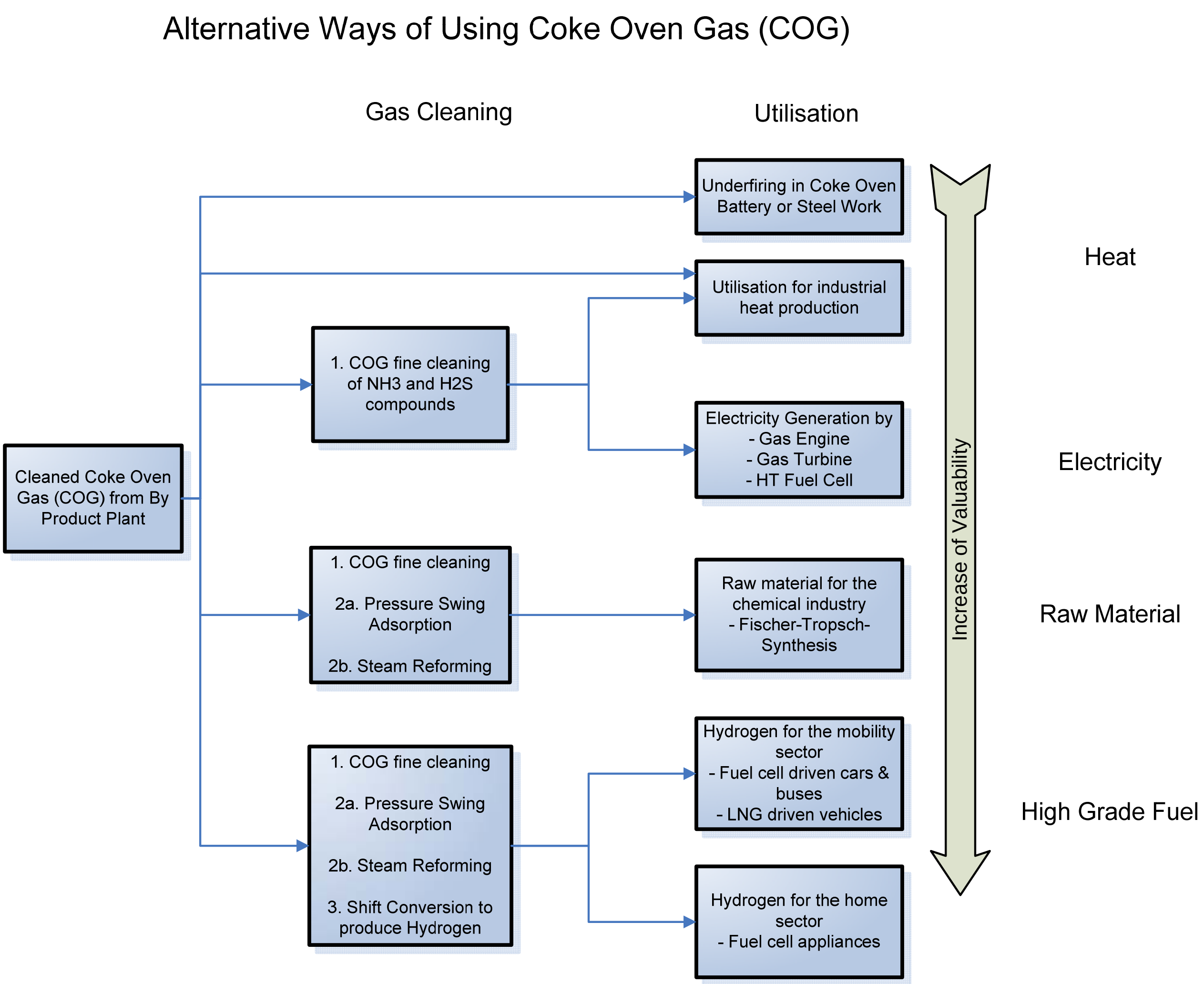

Figure 1. Alternative ways of using COG.

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2 OVERVIEW OF DESULPHURISATION PROCESSES

Generally the processes suitable for desulphurisation of COG can be subdivided into different methods:

- dry oxidation processes;
- wet oxidation processes;
- absorption/ stripping processes.

Table 1. Coke oven gas desulphurisation processes and their characteristics(1)

Wet oxidative processes		Absorption / stripping processes	
Name	**Description**	**Name**	**Description**
Stretford	H_2S is scrubbed from the coke oven gas by a sodium carbonate solution (Na_2CO_3) and elemental sulphur (S°) is yielded using vanadate (VO_3) as an intermediate. Regeneration of the scrubbing liquid takes place by aeration (O_2), using anthraquinone disulphonic acid (ADA) as an intermediate.	ASK* or Diamex	H_2S is scrubbed from the coke oven gas by a NH_3 solution. The NH_3 solution is derived from the NH_3 scrubber. The H_2S and NH_3 are stripped from the washing liquor by steam stripping and the vapours are led to a Claus plant or a sulphuric acid plant.
Takahax	Similar to the Stretford process, except that 1,4-naphthoquinone-2-sulphonic acid is used as an intermediate for the regeneration.	Vacuum Carbonate	H_2S (and also HCN and CO_2) is scrubbed from the COG with a sodium carbonate solution or a potassium carbonate solution (Na_2CO_3 or K_2CO_3). The potassium variant allows higher carbonate concentrations. The washing liquor is regenerated in a column, using high temperature and low pressure (0.12-0.14 bar). Acid gases are stripped from the liquor and can be treated in a Claus plant or a sulphuric acid plant.
Thylox	Sodium thioarsenate ($Na_4As_2S_5O_2$) binds the H_2S and regeneration is done by oxygen treatment. Elemental sulphur is yielded.	Sulfiban	Coke oven gas is scrubbed with monoethanolamine (MEA). NH_3 removal prior to H_2S removal is necessary to avoid pollution of the washing liquor. H_2S is stripped from the MEA solution using steam and can be treated in a Claus plant or a sulphuric acid plant. Insoluble organic S-compounds are removed from the MEA solution as solid waste.
Perox	The gas is scrubbed with an ammonia solution. Parabenzoquinone is used for sulphur oxidation and regeneration of the scrubbing liquor is done by oxygen.	DESULF	Virtually the same as the ASK-process, but the NH_3 is removed from the NH_3 / H_2S vapour in saturators, producing ammonium sulphate ($(NH_4)_2SO_4$).
Fumaks-Rhodacs	H_2S is oxidised by picric acid in the Fumaks-phase, yielding elemental sulphur. Cyanides are recovered in the Rhodacs phase.		

**ASK = Ammoniumsulphide Circuit Scrubber (Ammoniumsulphid-Kreislaufwäscher)*

Here, only the wet oxidation and the absorption/ stripping processes will be considered for comparison as they form the main types of desulphurisation processes for COG cleaning.
In Europe, the most commonly applied process is the absorptive process using an ammonia liquor to scrub the H_2S from the coke oven gas (Ammoniumsulphide Kreislaufwäsche (ASK) process or Diamex). The discharge of small wastewater flows to the biological treatment plant does not require any further treatment.
The second interesting absorptive process variant is the Vacuum Carbonate process commonly operated with potassium carbonate (due to the high CO_2 content in the

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COG) which has some tradition at West European coke plants and is used at Chinese coke plants.
The most commonly applied wet oxidative process (outside Europe) is the Stretford process. It is applicable in a wide range of desulphurisation capacities from 400 to 110,000 Nm^3/h COG.
Coke oven gas desulphurisation of both the wet oxidative and the absorptive type can be applied at new and existing plants. The choice depends on the cleaned coke oven gas specifications, environmental considerations, the integration within the gas cleaning plant, etc.
Wet oxidative processes have a better desulphurisation efficiency than absorptive processes. Wet oxidative processes can have an efficiency of > 99.9% achieving residual H_2S concentrations as low as 1 mg/Nm^3 in the coke oven gas. Absorptive processes do not usually exceed 95% desulphurisation efficiency and residual H_2S concentrations in the coke oven gas are usually around 300 mg/Nm^3 to 500 mg/Nm^3 COG.
However, any wet oxidative process used for desulphurising coke oven gas will also remove most of the hydrogen cyanide from the coke oven gas and form sodium thiocyanide. The sodium thiocyanide and the small amounts of sodium sulphate and thiosulphate formed by side reactions are not regenerated by the process and build up in the circulating liquor.
It is therefore necessary to purge a liquid stream to prevent salting out of the chemicals. In the case of the Stretford process, this discharge flow contains vanadium compounds, quinone and hydroquinone compounds (from ADA), thiocyanide and thiosulphate. Discharge of these components is undesirable from an environmental and economic point of view (water pollution and loss of expensive chemicals).
To reduce chemical consumption cyanic acid (HCN) can be removed prior to desulphurisation in a pre-washer using a sodium polysulphide or ammonium polysulphide solution. Pre-removal of HCN does not reduce the total volume of effluent produced.
Wastewater from wet oxidative desulphurisation processes is usually treated separately owing to the presence of compounds that have a detrimental effect on the biological wastewater treatment plant. In principle the following alternative methods have been developed in pilot scale and could be applied for the treatment of the wastewater purge stream:

- evaporative or spray drying;
- biological degradation;
- oxidative combustion;
- reductive incineration.

3 COG CLEANING PLANT CONFIGURATION FOR TCO CONSIDERATIONS

For the elaboration of the Total Cost of Ownership (TCO) the Stretford process, the ASK process and the Vacuum Carbonate process - representing the most common processes of their classes - will be taken into closer consideration.
In order to properly prepare the TCO comparison the boundaries of the processes have to be adjusted correctly. As the ASK process uses NH_3 scrubbing liquor and the Claus plant is designed also to crack NH_3 and HCN from the stripped NH_3/H_2S vapours in addition to sulphur production, the Stretford process has to be extended by an Ammonium Sulphate Unit taking care for the NH_3 in the COG prior to

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desulphurisation. For the same reason also the Vacuum Carbonate process includes an Ammonium Sulphate Unit taking care for the NH_3 in the COG prior to desulphurisation.
Hence, the correct plant configurations for the TCO comparison read as Table 2.

Table 2. COG cleaning plant configurations

Wet oxidative process		**Absorption / stripping process**	
Name	**Description**	**Name**	**Description**
Ammonium Sulphate Unit / Stretford Unit	H_2S (and also HCN) is scrubbed from the coke oven gas by a sodium carbonate solution (Na_2CO_3) and elemental sulphur (S°) is yielded using vanadate (VO_3) as an intermediate. Regeneration of the scrubbing liquid takes place by aeration (O_2), using anthraquinone disulphonic acid (ADA) as an intermediate. Configuration: • Ammonium Sulphate Unit (Spray Type or Bubble Type Saturator) • Stretford Unit By-Products: • Ammoniumsulphate ($(NH_4)_2SO_4$) • Elementary Sulphur (S°)	ASK* Unit / Claus Unit	H_2S (and also HCN) is scrubbed from the coke oven gas by an NH_3 solution. The NH_3 solution is derived from the NH_3 scrubber. The H_2S and NH_3 compounds are stripped from the washing liquor by steam stripping and the vapours are led to a Claus plant. Configuration: • H_2S / NH_3 -Scrubbing Unit (ASK) • Distillation Unit (Stripper- / Deacidifier) • Claus-Plant (Combined NH_3-Cracking / Elementary Sulphur Unit) By-Product: • Elementary Sulphur (S°)
		Ammonium Sulphate Unit / Vacuum Carbonate (Potash) Unit / Sulphuric Acid Unit	H_2S (and also HCN and CO_2) is scrubbed from the COG with a potassium carbonate solution (K_2CO_3). The washing liquor is regenerated in a column, using high temperature and low pressure (0.12-0.14 bar). Acid gases are stripped from the liquor and shall be treated in a sulphuric acid plant. Configuration: • Ammonium Sulphate Unit (Spray Type or Bubble Type Saturator) • Potash Scrubber and Vacuum Regenerator for scrubbing liquor • Sulphuric Acid Plant By-Product: • Ammonium Sulphate ($(NH_4)_2SO_4$)

**ASK = Ammoniumsulphide Circuit Scrubber (Ammoniumsulphid-Kreislaufwäscher)*

Please note that all units have been considered without redundancies of the main process equipment.
It is assumed that the above mentioned processes are well known from literature and need not to be described in this paper.(2)

4 COMPARISON OF TOTAL COST OF OPERATION (TCO) OF THE THREE PROCESSES

For the TCO comparison of the three processes the system configurations displayed in the Figure 2 have been selected.

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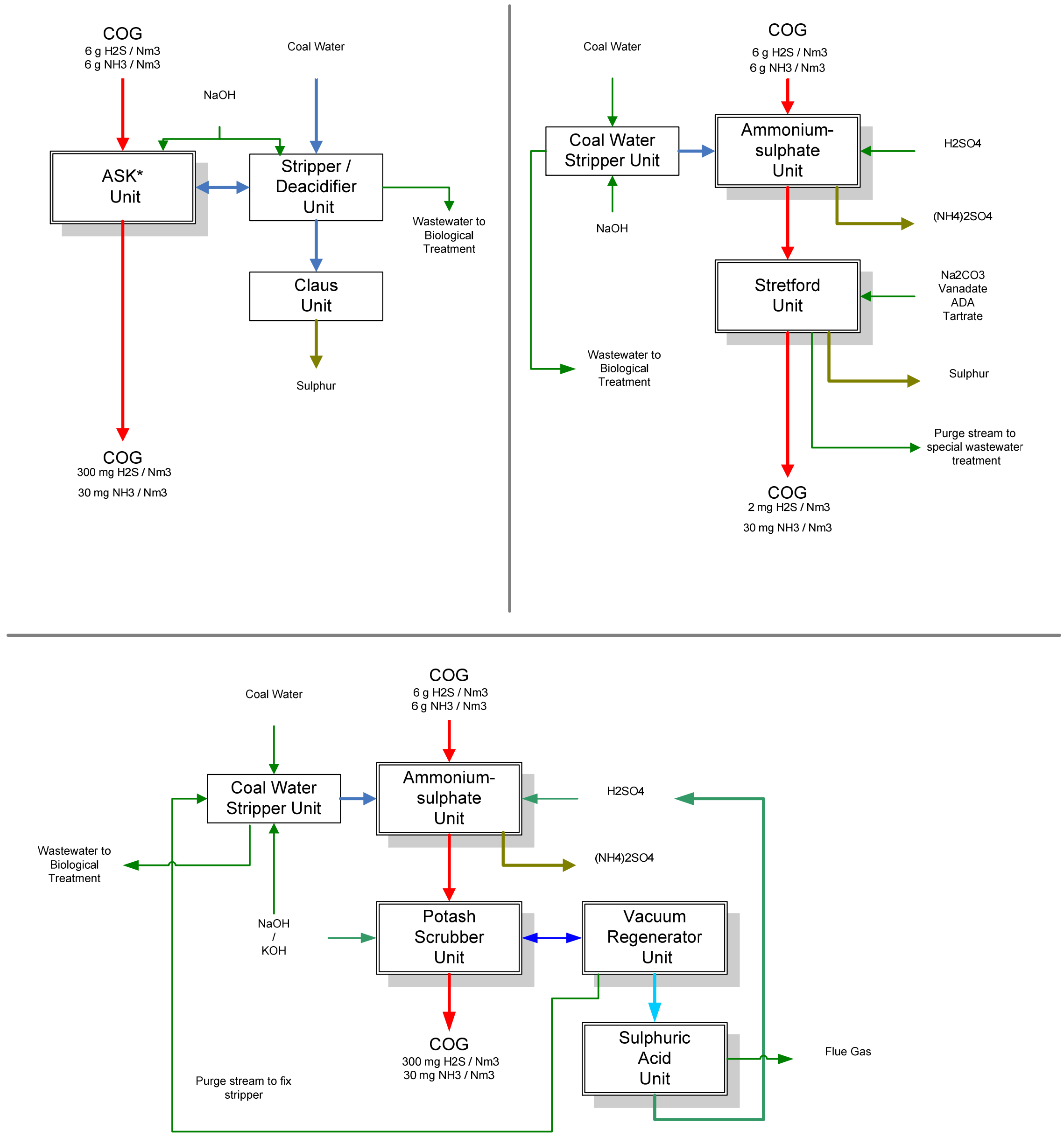

**ASK = Ammoniumsulphide Circuit Scrubber (Ammoniumsulphid-Kreislaufwäscher)*

Figure 2. System configurations.

Stripping of coal water has been considered for TCO in all three configurations. It leads to an additional stripping column in the Stretford and Vacuum Carbonate configurations, whereas in the ASK process the coal water is stripped in the already existing stripper column. Addition of caustic soda is required in the cases to strip fix ammonia, whereas in the Vacuum Carbonate process surplus caustic potassium will be used.

Moreover, a BTX/Naphthalene scrubber and stripping unit has principally to be taken into account for all three configurations. In the wet absorption process it is located between the Ammonium Sulphate and the Stretford unit, in the Vacuum Carbonate process it is located between the Ammonium Sulphate and the Potash Scrubber and in the ASK process it is commonly located after the NH_3 Scrubber. As the conditions are the same for all three configurations, the BTX/Naphthalene scrubbing and regeneration unit has not been taken into account for the TCO evaluation in the three configurations.

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The special wastewater treatment unit for the contaminated purge stream of the Stretford process has not been included in the TCO calculation, because reliable process data and costs could not be obtained. However, this treatment would lead to malus points in the TCO calculation for the wet oxidative process. The wastewater stream is loadedwith ca. 300 g/l thiocyanate [Hazard Code Xn (harmful to health)], 22.4 g/l thiosulphate [Hazard Code Xi (irritant)], 0.3 g/L vanadate [Hazard Code T (toxic)] und 0.6 g/l ADA [Hazard Code Xi (irritant)] and has to be treated with special care.[(3)]

Please not that all units have been assumed without redundancies of the main process equipment. This assumption definitely has an effect in terms of reduced overall plant availability. However, this is true for all configurations and can therefore be neglected in this TCO comparison.

The basis for the TCO evaluation is a by-product plant handling 42,000 Nm^3 COG/h containing

The data given for the Stretford process are based on operational data from RAG coke plant Grimberg, Germany, whereas the data for the ASK process are based on operational experience of various coke plants. The data of the Vacuum Carbonate process are derived from RAG coke plant Zollverein.

A comparison of the TCO is presented in the figures below. In the TCO costs for energy (steam, electricity), chemicals, maintenance and debt service are calculated in EURO cent per Nm^3 of COG and are matched with the revenues from the product sales.

Consideration of the personnel costs is difficult as the operation of the units are managed by the shifts that are responsible for the whole by-product plant. It is assumed as first approach that the personnel costs are similar in both configurations and can thus be eliminated from the TCO calculation.

As can be derived the net operation costs are different and in favour of the Vacuum Carbonate process route, followed by the ASK process route and the Stretford process route. The net operation costs amount to 1.25 €ct / Nm^3 COG for the Streford process route, 1.22 €ct / Nm^3 COG for the ASK process route and 0.83 €ct/Nm^3 COG for the Vacuum Carbonate process route.

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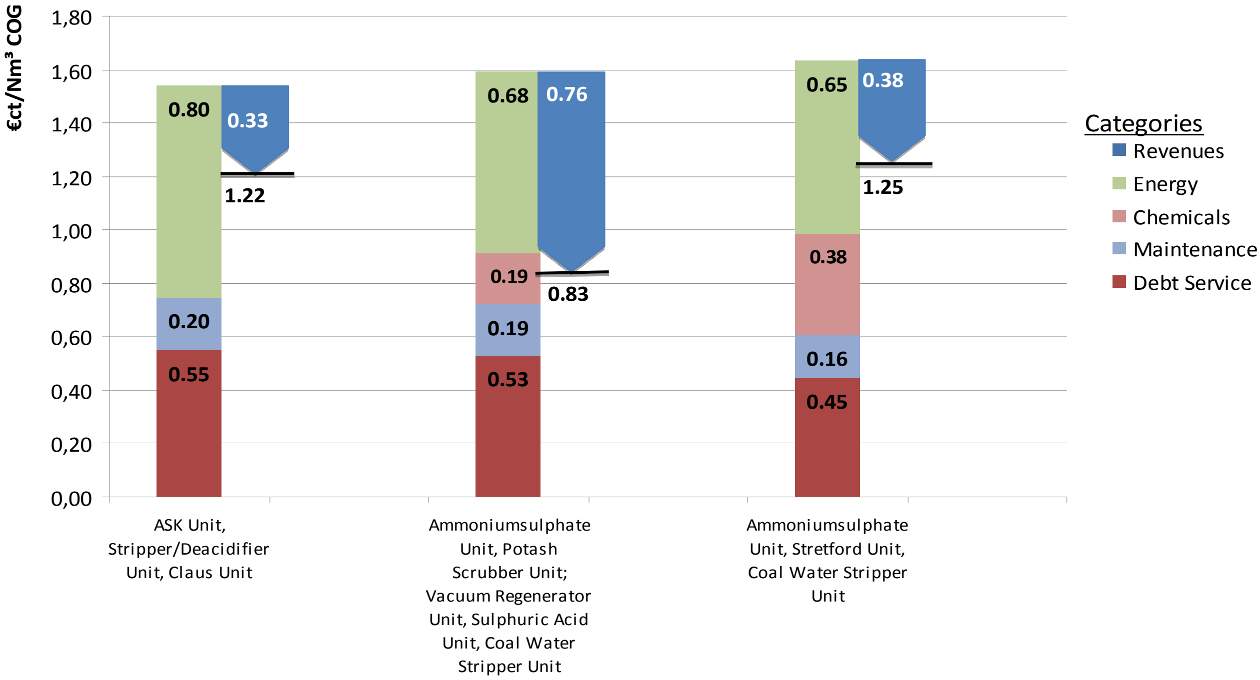

Figure 3. TCO comparison between ASK/ Stripping/ Claus Units, Vacuum Carbonate/ Ammonium Sulphate Units and Stretford/ Ammonium Sulphate Units.

The debt service (as investment indicator) range in the same magnitude for the ASK process route and the Vacuum Carbonate process route, which is on the one hand due to the number of units in the Vacuum Carbonate process route and the utilization of high alloy steel for reasons of corrosion resistance in the stripper / deacidifier columns of the ASK process. Debt service is lowest for the Stretford process route.

The maintenance costs range in the same magnitude for the ASK process route and the Vacuum Carbonate process route and are slightly lower for the Stretford process route as it is in all cases related to the investment costs.

However, distinct differences can be recognised in the consumption of chemicals and energy (i.e. operational costs). As the wet oxidation process route is mainly relying on chemical reactions the consumption of chemicals in the Ammonium sulphate and Stretford plant is high, and so are the costs of this category.

The ASK process route and the Vacuum Carbonate process are based on reversible physical absorption mechanisms, applying only small make-up streams. The reversibility is secured by application of steam to split and strip the weak temporary compounds resulting from the scrubbing. Thus more energy in terms of LP steam is consumed. In the Vacuum Carbonate process also electric energy for the vacuum pumps has to be taken into account. The energy costs of the Stretford process route reflect on the one hand the steam that is consumed for the coal water stripper and the autoclave and on the other hand the higher power consumption demanded by the electrical equipment such as pumps, blowers, centrifuges that are operated in the process.

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The chemicals utilized in the ASK process comprise caustic soda for stripping fix ammonia from the coal water. The same is used in the Vacuum Carbonate process route and the Stretford process route as well. Additionally the consumption of the sulfuric acid for the Ammonium sulphate plant and the loss of Stretford chemicals through the purge stream and through the contamination of the product sulphur account for the costs in the category "chemicals". The sulphuric acid plant in the Vacuum Carbonate process route generates most of the sulphuric acid that is used in the Ammonium sulphate plant and thus considerably reduces the net COG cleaning costs of this process route.

TCO calculations with variations of the H_2S load (6, 9 and 12 g/Nm^3) and COG flow (50,000 and 100,000 Nm^3/h) demonstrate that with increasing amount of H_2S the Ammonium sulphate / Stretford process becomes more expensive relative to the ASK process due to the higher chemical consumption. The same holds true for the increase of the COG flow as the Ammonium sulphate/ Stretford process has to be designed to handle the full flow of COG, whereas only the scrubbers in the ASK process have to be engineered accordingly. The rest of the process handles only vapours which volume flow is comparably less increasing than the increase of the COG flow.

As can be derived the net operation costs still remain in favour of the Vacuum Carbonate process route, followed by the ASK process route and the Stretford process route. The net operation costs amount to 1.30 €ct/Nm^3 COG for the Streford process route, 1.17 €ct/Nm^3 COG for the ASK process route and 0.88 €ct/Nm^3 COG for the Vacuum Carbonate process route.

With increasing amount of H_2S (6 to 8 g/Nm^3 COG) in the COG the net cleaning costs of the Vacuum Carbonate process route and the Streford process route increase due the higher consumption of steam/electric energy (Vacuum Carbonate) and chemicals (Stretford), whereas the net cleaning costs of the ASK process route are sinking due to higher production of high quality sulphur (higher revenues) while the steam consumption remains at an unchanged level.

The revenues mitigate the operational costs distinctly in case proper sale prices can be negotiated. Small variations in the revenues from product sales have a decisive effect on the TCO assessment. Commonly the quality of the Stretford sulphur is of deteriorated quality and is difficult to sell. If it comes worse and the Stretford sulphur can not be sold, it has even to be disposed of as dangerous (toxic) waste. In this TCO comparison a zero sale price for Stretford sulphur compared to the high quality, bright yellow sulphur of the Claus plant has been consiudered.

The quality of the Claus sulphur is usually matching the quality demands of the chemical industry and is, hence, sold at a comfortable price.

The ammonium sulphate is offered as an acid, sulphur containing fertilizer in the agricultural industry. Depending on the need for acid fertilizers the price may vary from season to season depending on the crops planted in the respective season. Actually the price for ammonium sulphate is acceptable in Europe as sulphur containing (acid) fertilizers are used again in agriculture after the negative effects of acid rain (NOx, SOx emissions from industry and power generation) on soil have been remedied by time. In this TCO the revenues of the wet oxidation process route are dominated by the sale of ammonium sulphate.

Figure 4. Stretford sulphur after autoclave (left) / Claus sulphur (right).

The sulphur production from the Stretford unit is less than from the Claus-plant as it considers a slip stream of sulphur needed for the generation of the polysulphide for the HCN-scrubber.
The whole TCO calculation is based on European costing and prices. For this reason even the LP steam that is required for the stripping and heating processes has been associated with a price contributing sincerely to the operational costs.
In integrated steel plants LP steam is usually available in surplus quantities and free of charge from the steam network. Chemicals and electricity, however, have to be procured from external sources.

5 CONCLUSIONS

The optimal COG cleaning process has to be carefully selected depending on the COG purity requirements in view of the perspective final utilization of the gas.
Wet oxidative processes such as the Stretford process in combination with an ammonium sulphate process require expensive chemicals for the gas cleaning. The cleaning efficiency is better than the absorption / stripping process will yield. Depending on the revenues to be received from sales of sulphur and ammonium sulphate products the Total Cost of Ownership (TCO) clearly shows the following ranking (left side = lowest costs):

Vacuum Carbonate process route < ASK process route < Stretford process route

In case of free of charge availability of LP steam from the steam network in an integrated steel plant, the TCO becomes distinctly lower for all processes, without changing the ranking.
Absorption/ stripping processes such as the ASK process and the Vacuum Carbonate process mainly consume LP steam for the stripping process. In case of free of charge availability of LP steam from the steam network in an integrated steel plant, the ASK/ Vacuum Carbonate process routes becomes much more cost efficient compared to the Stretford process route. However, the cleaning efficiency is of 300 mg H_2S / Nm^3 COG, 30 mg NH_3 / Nm^3 COG) is well in the limit of meeting the stringent environmental regulations in most countries. The quality of the Claus sulphur, however, is much better and prone to higher revenues when sold to the chemical industry.
Table 3 summarizes the main advantages and disadvantages of the three process routes under comparison on a glance.

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Table 3. Comparison of one Wet oxidative process and two Absorption / stripping processes

Wet oxidative process		**Absorption / stripping process**	
Name	**Description**	**Name**	**Description**
Stretford / Ammonium sulphate process	H_2S (and also HCN) is scrubbed from the coke oven gas by a sodium carbonate solution (Na_2CO_3) and elemental sulphur (S°) is yielded using vanadate (VO_3) as an intermediate. Regeneration of the scrubbing liquid takes place by aeration (O_2), using anthraquinone disulphonic acid (ADA) as an intermediate. Advantages: • Good cleaning efficiency • High quality Ammoniumsulphate with high revenues • No HP-scrubbing required Disadvantages: • Higher operating costs • NH_3 and HCN pre-scrubbing required • Catalyst as consumable required • Produces toxic sludges • Low Quality of Sulphur S° not saleable, may be extra cost for disposal in special land fill • Contaminated wastewater streams need special treatment • Susceptible for contamination • Dependence on suppliers for catalyst and ADA (consumables)	ASK* / Stripping / Claus process	H_2S (and also HCN) is scrubbed from the coke oven gas by a NH_3 solution. The NH_3 solution is derived from the NH_3 scrubber. The H_2S and NH_3 are stripped from the washing liquor by steam stripping and the vapours are led to a Claus plant. Advantages: • Good cleaning efficiency • Lower operating costs • No consumable catalyst required • NH_3-scrubbing included • High quality Sulphur S° with high revenues • No contaminated wastewater; wastewater can be directly delivered to the biological treatment plant Disadvantages: • HP-scrubbing necessary to achieve a H_2S concentration of below 2 mg/Nm^3 in the clean gas (only required for extraordinary applications)
		Vacuum Carbonate (Potash)	H_2S (and also HCN and CO_2) is scrubbed from the COG with a potassium carbonate solution (K_2CO_3). The washing liquor is regenerated in a column, using high temperature and low pressure (0.12-0.14 bar). Acid gases are stripped from the liquor and can be treated in a sulphuric acid plant. Advantages: • Good cleaning efficiency • Low operating costs • No consumable catalyst required • High quality Ammoniumsulphate with high revenues • No contaminated wastewater; wastewater can be directly delivered to the biological treatment plant Disadvantages: • HP-scrubbing necessary to achieve a H_2S concentration of below 2 mg/Nm^3 in the clean gas (only required for extraordinary applications) • Requires potassium carbonate solution (K_2CO_3).

**ASK = Ammoniumsulphide Circuit Scrubber (Ammoniumsulphid-Kreislaufwäscher)*

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Concluding this paper it can be stated that the absorption/stripping processes (such as the the ASK process and the Vacuum Carbonate route) are cost efficient and at the same time an environmentally sound way of cleaning COG.
Today, in new and modernized coke making plants the most commonly applied process for the desulphurization of coke oven gas is the ASK process in combination with the Claus process.

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3 Material Data Safety Sheets acc. 1907/2006/EG, Article 31, are available via http://www.eusdb.de